

Influence of the initial fluoropolymer in polystyrene sulfonic acid containing radiation-grafted membranes

Nadia Walsby¹, Franciska Sundholm¹, Sami Hietala, Tanja Kallio² and Göran Sundholm²

¹Laboratory of Polymer Chemistry, University of Helsinki, PB 55, 00014 HY Helsinki, Finland

²Laboratory of Physical Chemistry and Electrochemistry, Helsinki University of Technology, PB 6100, 02015 HUT, Finland

Radiation-grafted membranes have been much investigated as potential polymer electrolytes for fuel cells. The appeal of this approach lies in the flexibility of the process and in the low costs involved. Typically a starting material is chosen, irradiated, grafted with styrene and then sulfonated. The properties of the membranes are studied as a function of the amount of polystyrene sulfonic acid (PSSA) added. However, as the preparation conditions vary from case to case it is impossible to compare results and the influence of the initial fluoropolymer is unclear. To address this, a series of membranes based on various fluoropolymers with similar PSSA contents was prepared in the same way and characterised. Some of the properties are given in Table 1.

Tensile tests revealed that the properties of the grafted and sulfonated materials at intermediate water contents differed much less than those of the initial materials. The influence of the matrix polymer on the water uptake of the membrane was found to be dependent on the pretreatment of the samples. The water uptake from liquid water decreased with increasing matrix crystallinity. However, samples first dried over P₂O₅ and then placed at 100 % RH all had the same water uptake (Fig. 1). Drying appeared to cause some shrinkage, which was irreversible at room temperature. DSC data showed that the differences in water uptake were due to differences in freezing water content. Membranes with higher water uptakes appeared to have larger pores.

Conductivities were of the same order as those of the Nafion materials and varied with the water uptake. PFG-NMR measurements showed that, despite considerably higher absolute water contents, the water self-diffusion coefficients in the radiation-grafted materials were no higher than those in Nafion 117 at a given water molecules per sulfonic acid group ratio (λ). Proton diffusion coefficients calculated from the conductivity data showed that, at intermediate λ , proton diffusion was slower than water self-diffusion in radiation-grafted membranes whereas in Nafion 117 the proton and water self-diffusion coefficients were similar. When considered along with differences in the T_{1H} relaxation times, this suggests differences in the morphology of the hydrophilic domains in Nafion and radiation-grafted membranes, the sulfonic acid/water regions possibly being more homogeneous in the latter.

The electrochemical characteristics are discussed further in the abstract by Kallio *et al.* entitled “Different Radiation Grafted Ion-exchange Membranes for Polymer Electrolyte Fuel Cell”

Table 1. Membrane properties

matrix	DOG %	d wet μ m	matrix cryst. %	w.u. from L g/g	IEC meq/g	σ mS/cm 100 % RH rt
PVDFa	39	130	40	0.79	1.83	66
PVDFb	39	70	41	0.67	1.83	72
ETFE	31	90	15	0.82	1.51	43
PVDF-co-HFP 6%	39	130	27	0.99	1.81	63
PVDF-co-HFP 15%	40	120	20	1.22	1.94	110
FEP	34	145	15	1.00	1.80	108
Nafion 117	-	210	-	0.35	0.89	51
Nafion 105	-	150	-	0.50	1.00	56

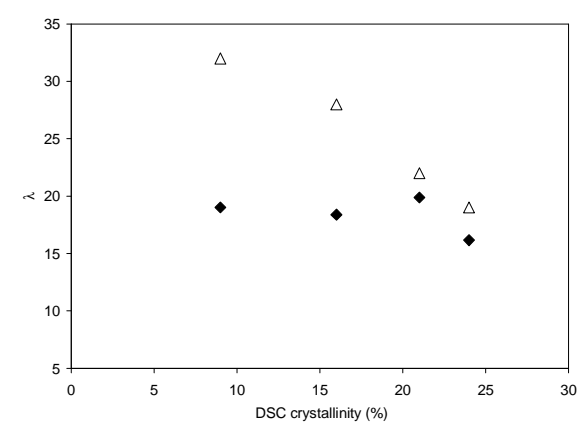


Fig. 1. Number of water molecules per sulfonic acid group absorbed from liquid water after boiling (Δ) and at 100 % RH after drying (\blacklozenge)

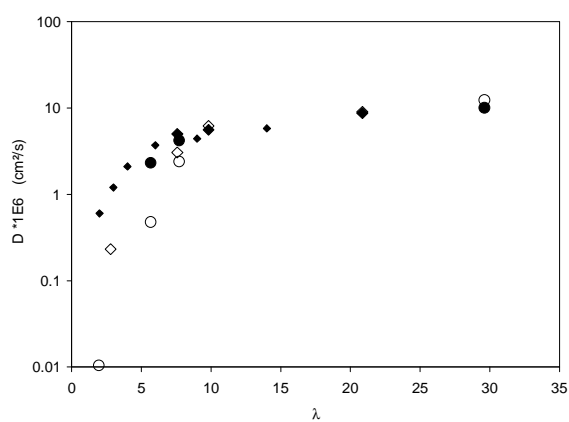


Fig. 2. Water self-diffusion coefficient in Nafion 117 (\blacklozenge) and FEP-g-PSSA (\bullet); proton diffusion coefficient in Nafion 117 (\diamond) and FEP-g-PSSA (O).